

1 HYDROLYZABLE PREPOLYMERS FOR EXPLOSIVE AND
2 PROPELLANT BINDERS

3
4 STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR
5 DEVELOPMENT

6 The invention described herein may be manufactured and used by or
7 for the government of the United States of America for governmental
8 purposes without the payment of any royalties thereon or therefor.

9 BACKGROUND OF THE INVENTION

10 1. Field of the Invention

11 The present invention includes chemically curable prepolymers used in binders for
12 explosives and propellants. More particularly, the prepolymers include a formal component
13 to increase the hydrolyzing properties of the prepolymers and formed binders from the
14 prepolymers. The prepolymers and binders are easily degraded to recover
15 explosive/propellant chemical components.

16 2. Brief Description of the Related Art

17 Chemically cured binders currently used in explosives and propellants are difficult
18 to degrade at the end of their life-cycle. With the lack of easy degradation, the recovery of
19 valuable components of the energetic composition is hindered.

1 Several types of binders are known in explosives and propellants. Polybutadiene or
2 polyether structures contain no readily degradable groups. Binders containing ester groups
3 alone, such as polycaprolactone or carboxy-terminated prepolymers cured with epoxides,
4 possess hydrolyzable ester groups, but the conditions for hydrolysis, *i.e.*, time, temperature,
5 are severe.

6 There is a need in the art to provide binders for energetic materials with prepolymers
7 containing more readily hydrolyzable moieties in the backbone to improve the degradability
8 of explosive and propellant binders. The present invention addresses this and other needs.

9 SUMMARY OF THE INVENTION

10 The present invention includes a degradable prepolymer for explosive and propellant
11 compositions having increased hydrolyzability comprising at least one -O-CH₂-O- linkage
12 within the backbone of the prepolymer.

13 The invention also includes a degradable polymer product formed by the process
14 comprising the steps of providing a degradable prepolymer for explosive and propellant
15 compositions having increased hydrolyzability comprising at least one -O-CH₂-O- linkage
16 within the backbone of the prepolymer and curing the degradable prepolymer with a
17 polyisocyanate.

18 Additionally, the present invention includes a degraded polymer product formed by
19 the process comprising the steps of providing a degradable prepolymer for explosive and

1 propellant compositions having increased hydrolyzability comprising at least one -O-CH₂-O-
2 linkage within the backbone of the prepolymer and reacting the degradable prepolymer with
3 a degrading chemical composition.

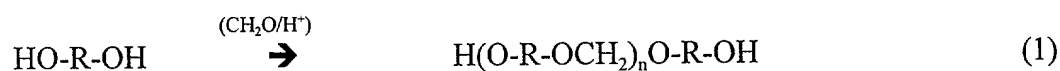
4 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

5 The present invention includes degradable prepolymers used to form binders in
6 explosive and propellant compositions. The degradable prepolymers have increased
7 hydrolyzability resulting from the incorporation of a formal unit, or -O-CH₂-O- structure,
8 within the backbone of the prepolymers. The prepolymers containing hydrolyzable groups
9 within the polymer chain are used to create the binders, while providing hydroxy groups at
10 the prepolymer chain ends. By chemically curing the hydrolyzable prepolymers, binders are
11 created that are useful in energetic materials, such as explosives and propellants. The
12 prepolymers comprise non-energetic materials.

13 The present invention provides formal prepolymers with improved hydrolyzability,
14 which may be adjusted for particular needs. As such, the ease of hydrolyzability of the
15 prepolymers, or formed binders, is adjustable for particular uses directed to specific shelf-
16 life, degradability, type of explosive, ease of use, and other like operational factors for
17 explosives or propellants, with the proper degree of hydrolyzability for a particular use
18 determinable by those skilled in the art.

19 In general terms, the polyformals are made by condensation of diols with

1 formaldehyde and contain the formal group as the hydrolyzable moiety, as shown in equation
2 1, below:



7 with R representing a carbon or carbon/heteroatom chain, and n representing the number of
8 repeat units.

9 Examples

10 Examples 1 and 2 show the preparation of the prepolymers of the present invention
11 which are useful to form binders for explosives and propellants. The hydrolyzability of the
12 uncured prepolymers was tested by stirring a sample dissolved in water or, when not water-
13 soluble, in dichloromethane or tetrahydrofuran, with 1.0 N hydrochloric acid at room
14 temperature. After approximately 24 hours, the molecular weight of the recovered material
15 was determined by gel permeation chromatography (GPC) analysis. Examples 3 and 4 show
16 that the prepolymers are curable with a conventional polyisocyanate such as Desmodur N-
17 100.

18 Example 1

19 **Preparation of Poly(PEG-400 formal) (hydroxy-terminated)-** A mixture of 10.0g
20 of polyethyleneglycol (molecular weight 400, PEG-400) and 0.75g of trioxane was cooled
21 with ice, and 3.0mL of borontrifluoride etherate was added dropwise with stirring. The

1 mixture was allowed to warm to room temperature (approximately 20°C) and stirring was
2 continued for a total of 24 hours. The mixture was diluted with 25mL of ether, poured into
3 a solution of 5g of sodium hydrogencarbonate and 3mL of 30% hydrogen peroxide in 50mL
4 of water, and the total stirred vigorously for 1 hour. The phases were separated, the aqueous
5 phase was saturated with sodium chloride and extracted with 25mL of ether, the combined
6 ether phases were dried with magnesium sulfate and stripped on a rotary evaporator to give
7 9.5g (92%) of a colorless oil. Gel permeation chromatography (GPC) analysis and
8 comparison with poly(ethyleneglycol) standards showed the peak molecular weight of this
9 polymer to be approximately 3,500.

10 Example 2

11 **Preparation of Poly(PCL-500 diol formal) (hydroxy-terminated)-** A mixture of
12 7.36g of poly(caprolactone)diol (molecular weight 530, PCL-500), 0.42g of p-formaldehyde,
13 and 3.5mL of dichloromethane was cooled in an ice-bath, and 1.39mL of boron trifluoride
14 etherate was added with stirring. The mixture was stirred at room temperature
15 (approximately 20°C) for 24 hours, was diluted with 20mL of dichloromethane, poured into
16 a solution of 2.8g of sodium hydrogen carbonate in 28mL of water, and the total agitated for
17 0.5 hours. The dichloromethane phase was dried with magnesium sulfate and freed from
18 solvent to give 7.5g (100%) of a light brown oil which solidified on standing. GPC analysis
19 and PEG standards indicated a peak molecular weight of 3,600.

Example 3

Curing of Poly(PEG-400 formal) with Desmodur N-100- The polymer obtained in Example 1 was used in an amount of 1.0g and was mixed with 1g of di-n-butylphthalate, 0.005g of triphenylbismuth, and 0.136g of Desmodur N-100 (NCO:OH ratio 1.1:1 + 10% excess NCO). The mixture was stirred with a glass rod until homogeneous and was then stored at 65°C. After 4 days, an elastomeric gumstock had formed.

Example 4

Curing of Poly(PCL-500 diol formal) with Desmodur N-100- The polymer obtained in Example 2 was used in an amount of 1.03g and was mixed with 1g of di-n-butylphthalate, 0.005g of triphenylbismuth, and 0.136g of Desmodur N-100 (NCO:OH ratio 1.1:1 + 10% excess NCO). The mixture was stirred with a glass rod until homogeneous and was then stored at 65°C. After 4 days, an elastomeric gumstock had formed.

The prepolymers forming the binder comprise molecular weights suitable for processing, while enabling the formed binder to provide sufficient structural integrity to bind explosive and/or propellant compositions. The molecular weight of the prepolymers may range, for example, from about 2,000 to about 10,000; 2,500 to about 9,000; or 3,000 to about 8,000, with the proper molecular weight determinable by those skilled in the art for specific polymers and types of compositions. Monomer units within the prepolymers

1 typically may range in molecular weight, for example, of from about 300 to about 1000; or
2 about 400 to about 500. For the prepolymer, typically from about two to about ten -O-CH₂-
3 O- linkages; or from about five to about eight -O-CH₂-O- linkages are used within the
4 backbone of the prepolymer.

5 Preferred hydroxy-terminated prepolymers include poly(PEG-400 formal) having
6 a polyethylene glycol component with a molecular weight of about 400 and poly(PCL-500
7 diol formal) having a polycaprolactone component with a molecular weight of about 500.

8 Poly(PEG-400 formal) was shown to hydrolyze completely upon treatment with 1 N
9 hydrochloric acid at room temperature for 24 hours. The ease of the hydrolysis of the
10 poly(PEG-400 formal) was found to be greater than that of poly(PCL-500 diol formal),
11 however the poly(PCL-500 diol formal) was found to have excellent hydrolyzability.

12 When forming binders for energetic materials, the curing agent must be capable of
13 reacting with the terminal groups on the prepolymers. With the hydroxyl terminal groups,
14 the di- or polyisocyanates are the preferred curing agents. Examples of suitable isocyanates
15 include arylene polyisocyanates such as toluene diisocyanates; meta-phenylene diisocyanate;
16 4-chloro-1, 3-phenylene diisocyanate; methylenebis-(4-phenyl isocyanate); 1, 5-naphthalene
17 diisocyanate; 3, 3'-dimethoxy -4, 4'-biphenylene diisocyanate; 3, 3'-diphenyl-4,
18 4'-biphenylene diisocyanate; triphenylmethane triisocyanate; and alkylene poly-isocyanates
19 such as methylene; ethylene; propane-1, 2; butane-1, 3; hexane-1, 6 and cyclohexane-1, 2

1 diisocyanates. Mixtures of poly-isocyanates may also be used. Isophoron diisocyanate
2 (IPDI) and Desmodur N-100 isocyanate curing agent, a commercial product of the Bayer
3 Corp., Pittsburgh, Pa., are most often used. The formed prepolymers possess a functionality
4 suitable for curing with isocyanates, with a preferred functionality of from about 1.7 to about
5 2.3, more preferably with a functionality of approximately 2.

6 The prepolymers of the present invention are hydrolyzable by the action of dilute
7 aqueous acid at room temperature. Degradation of the prepolymers or formed binders may
8 be performed by contact with an acidic degrading chemical composition, such as a dilute
9 acid. Contact between the prepolymers and degrading composition is enhanced with
10 agitation, such as stirring or mixing. The dilute acid may include suitable concentrations,
11 such as from about 2.0 N or less, 1.5 N or less, or 1.0 N or less, with the proper concentration
12 for a particular polymer or binder determinable by those skilled in the art.

13 Polymers of the present invention permit convenient processing of explosives or
14 propellant that have outlasted their useful shelf life. The present invention provides
15 telechelic poly(ethyleneglycol) and poly(caprolactone) polymers with hydrolyzable formal
16 groups in the backbone that can be degraded by the action of dilute acidic compositions.

17 The foregoing summary, description, and examples of the present invention are not
18 intended to be limiting, but are only exemplary of the inventive features which are defined
19 in the claims.